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The triplet-triplet absorption and polarization spectrum of anthracene was obtained over the 390 to 540 nm spectral region. Photoselection spectroscopy was employed. For excitation the 379.5/385.3 nm lines from a cw argon ion laser were used. The obtained polarization spectrum was uniformly, negatively polarized over the entire 390 to 540 nm spectral region, with no sign of the positively polarized $^3A_{1g} \leftarrow {}^3B_{2u}^+$ transition.

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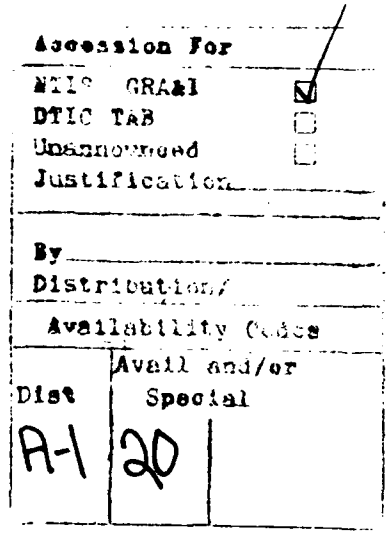

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RESEARCH NOTE

Triplet–triplet absorption and polarization spectra of anthracene

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INTRODUCTION

Although the T–T absorption spectrum of anthracene is among the most widely studied T–T absorption spectra of any organic compound [1], the measurement of the polarization of this spectrum has proved to be difficult [2]. The T–T absorption spectrum of anthracene consists of a strong transition located in the near-UV/violet portion of the spectrum. It consists of three bands, with the 0,0 band located at 430 nm. This strong band is long-axis-polarized and has been assigned to the ${}^3B_{1g}^- \leftarrow {}^3B_{2u}^+$ transition [3, 4]. A weaker band with vibrational structure stretches from about 450 to 540 nm. It has been suggested that this band presents the long-axis-polarized ${}^3A_{1g}^- \leftarrow {}^3B_{2u}^+$ transition [2, 5]. A much weaker band extends to about 900 nm and has been assigned to a forbidden transition [6].

The difficulty in obtaining polarization spectra results from the overlap of the two differently polarized singlet–singlet (S–S) bands, namely the ${}^1A_{1g} \leftarrow {}^1B_{2u}$ and ${}^1A_{1g} \leftarrow {}^1B_{3u}$ transitions. Exciting with either the 351/554 nm lines from a krypton ion cw, or with the 325 nm line from a cadmium/helium cw laser, results in a depolarized T–T absorption spectrum. However, employing the 379.5/385.3 nm lines from an argon ion cw laser produced a clearly polarized spectrum.

Apparently, sufficient laser radiation is adsorbed at the onset of the 0,0 band at 374 nm [7] of anthracene to produce considerable triplet optical density OD_T, provided a sufficiently high solute concentration is used. Not only was the triplet optical density sufficient to record the T–T absorption spectrum over the entire 390–540 nm spectrtal region, but also the polarization of this spectrum.

EXPERIMENTAL

Chemicals

Anthracene, 99.9% "Gold Label", was obtained from Aldrich Chemical Co. and 2-methyltetrahydrofuran from Lancaster Synthesis Ltd.

As glassy solvent for anthracene, we switched from the ethanol/methanol mixture to 2-methyltetrahydrofuran. This solvent allows anthracene to dissolve at higher concentrations (about 2×10^{-4} molar) than the ethanol/methanol mixture (about 0.6×10^{-4} molar [8]). Higher solute concentrations produce higher triplet optical densities.

Apparatus

The same equipment was employed to measure the T–T absorption and polarization spectra as in Refs [9, 10]. The high reflector/output coupler minors for the 379.5/385.3 nm ion argon cw laser lines were purchased from Spectra Physics.

RESULTS AND DISCUSSION

The T–T absorption spectrum and its polarization are presented in Fig. 1. Measurement accuracy of the OD_T values as well as the P values was rather high because anthracene dissolved in 2-methyltetrahydrofuran was rather stable photochemically under excitation with the 379.5/385.3 nm argon ion laser lines. Each P value was measured three times and the average of these data is presented Fig. 1. The P values should have an accuracy of about ± 0.02. The measured OD_T values of anthracene were converted to molar triplet extinction coefficients by using the ε_T value at 430 nm obtained by McCLURE's method [8, 11].

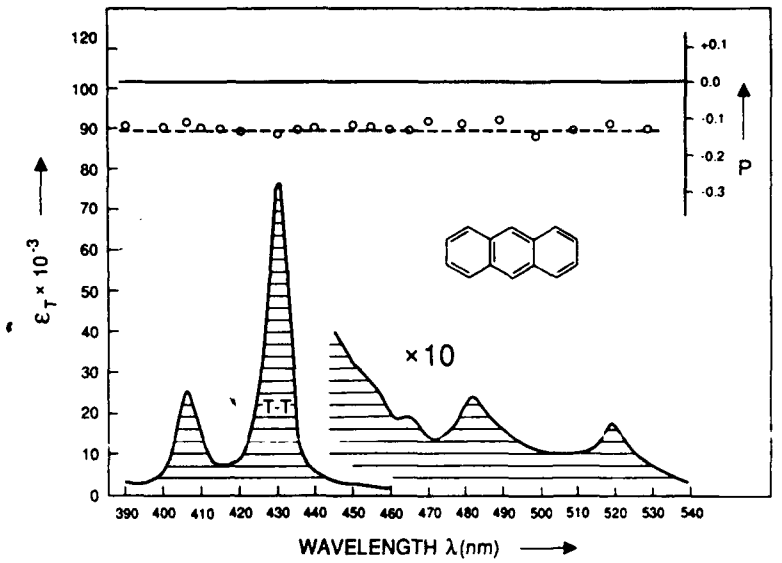

Fig. 1. Triplet–triplet absorption and polarization spectrum of a 2×10^{-4} molar solution of anthracene in 2-methyltetrahydrofuran, recorded at the temperature of liquid nitrogen.

From the polarization curve shown in Fig. 1, it is apparent that there is no trace (dip) indicating the presence of the positively polarized ${}^3A_{1g}^- \leftarrow {}^3B_{2u}^+$ transition. There are three explanations for the absence of this transition over the spectral region we studied:

(a) The ${}^3A_{1g}^- \leftarrow {}^3B_{2u}^+$ transition is located directly under the strong 0.0 band at 430 nm of the ${}^3B_{3g}^- \leftarrow {}^3B_{2u}^+$ transition. Its weaker intensity does not alter the negative degree of polarization P of the ${}^3B_{3g}^- \leftarrow {}^3B_{2u}^+$ transition.
(b) The ${}^3A_{1g}^- \leftarrow {}^3B_{2u}^+$ transition is located to the short-wavelength side of the 0.0 band at 430 nm and is of weak intensity.
(c) The ${}^3A_{1g}^- \leftarrow {}^3B_{2u}^+$ transition is exceptionally weak and is buried under the weak, negatively polarized forbidden transition(s) stretching from about 450 to 540 nm.

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